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Editors of Physical Review B

Grenoble, January 12, 2000

Dear Editors,

We would like to submit our manuscript entitled *"Dielectric response of charge induced correlated state in quasi-one-dimensional conductor $(TMTTF)_2PF_6$"* for publication in Phys. Rev. We previously submitted it to Phys. Rev. Lett. (code number LH7335).

The delay for resubmission has been caused by difficulties in communication between co-authors, one at Moscow, another visiting Japan during several weeks. We would like, however, the original received date to be retained. The manuscript has been amended according to the referee comments as described below :

Referee A

1) We modified our description of the extended Mott-Hubbard model for half-filled bands (bottom of page 2) taking into account both the on-site interaction (U) and the near-neighbor interaction (V).

2) The $2k_F$ lattice fluctuations coupled to the lattice are observed at much lower temperature (below 60 K) than the large increase of the dielectric permittivity. We have rewritten the beginning of the discussion part, page 6, to make this point more clear.

Referee B

1) These organic conductors are very fragile and cracks may reflect significant strain when the cooling rate is too fast and/or the sample holding too tight. We used all the care possible for avoiding cracks in our crystals and thus measuring bulk properties.

2) There is no evidence in $(TMTTF)_2PF_6$ of a structural phase transition affecting the main Bragg reflections. The tentative explanation of our data is the occurrence of a superstructure ($4k_F$) transition. Such a transition could be very likely detected from NMR experiments.

Yours sincerely,

P. MONCEAU

Dielectric response of charge induced correlated state in the quasi-one-dimensional conductor $(TMTTF)_2PF_6$

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Abstract

Conductivity and permittivity of the quasi-one-dimensionsional organic transfer salt $(TMTTF)_2PF_6$ have been measured at low frequencies ($10^3 - 10^7$ Hz) between room temperature down to below the temperature of transition into the spin-Peierls state. We interpret the huge real part of the dielectric permittivity (up to 10^6) in the localized state as the realization in this compound of a charge ordered state of Wigner crystal type due to long range Coulomb interaction.

71.30+h, 71.10Hf, 77.22Gm, 75.30Fv

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I. INTRODUCTION

Conductors formed of linear chains of organic molecules tetramethyltetrathiafulvalene (TMTTF) or tetramethyltetraselenafulvalene (TMTSF) with a general formula $(TMTCF)_2X$ with C = Se, S and X the interchain counterion = ClO_4, PF_6, Br, ... have been intensively studied these last years because they exhibit a rich variety of cooperative phenomena including superconductivity, antiferromagnetism (AF), spin density wave (SDW), spin-Peierls state (SP), charge localization [1]. While the Bechgaard $(TMTSF)_2X$ salts display a metallic behaviour down to low temperature where a transition in a SDW state occurs below ~ 12 K, $(TMTTF)_2X$ salts exhibit a charge localization in the temperature range of 100–200 K, with a maximum in conductivity at T_ρ and a thermally activated variation below T_ρ [2,3], revealing strong Coulomb interaction effects in these sulfur salts.

Quasi-one-dimensional conductor $(TMTTF)_2X$ consists of molecular chains (along the highest conductivity axis) with two electrons per 4 molecules which corresponds to 1/4 filling in terms of holes. These molecular chains are slightly dimerized due to intermolecular interaction. As a result, with decreasing temperature a dimerized gap $\Delta\rho$ opens with effective 1/2 filling of the upper conduction band. Two intermolecular transfer integrals along molecular stacks t_1 and t_2 have to be considered [4]. Quantum chemistry calculations show that in $(TMTTF)_2PF_6$ the dimerization decreases with decreasing temperature and at low temperatures t_1/t_2 ratio is about 1.1 - 1.2 [4].

As was shown in several of theoretical and experimental works, between many factors which determine the properties of $(TMTTF)_2X$ type salts, electron-electron correlation phenomena play the leading part [1,4–13]. In this context two types of theoretical models have been essentially developed. In the frame of the so-called g-ology models [8,10,14] the electron-electron correlations are considered as a perturbation to the one-electron approach. These models have been used for describing the low energy properties of these salts which exhibit the features of a Luttinger liquid rather than a Fermi liquid [14].

The second group of models includes the various versions of the Hubbard model [9–13,15].

Extended Hubbard model takes into account the interaction between charge carriers on the site of host lattice (on-site interaction) with characteristic energy U as well as the interaction between charge carriers on the neighboring sites (near-neighbor interaction) with characteristic energy V. In the case of $(TMTTF)_2X$ compounds, at temperatures above the transition into spin ordered states, the electron-electron interaction is determined by long range Coulomb interaction and it is stronger than spin interaction. This is one of the reason of spin-charge separation observed in such 1D-conductors [1]. In the frame of extended Hubbard model it was shown that the dimerized energy gap is strengthened taking into account the on-site and near-neighbor interactions [9]. At the same time the spectrum of spin exitations remains gapless which also corresponds to spin-charge separation.

One important result of the extended Hubbard model approach concerns the formation of a $4k_F$ CDW superlattice of Wigner crystal type in such 1D compounds with decreasing temperature. Using Monte Carlo technique it was shown that, for large enough U and V magnitudes, strictly on-site interaction results only in a weak $4k_F$ CDW, while long range Coulomb near-neighbor interaction can produce a CDW singularity at $4k_F$ [9]. Analogously, using mean field approximation [13] it was recently shown that for one-dimensional molecular chain with and without dimerization the form of the developed superstructure depends considerably on the magnitude of near-neighbor interaction V: at V above some critical value V_c a $4k_F$ CDW superstructure occurs with charge disproportionation depending on V. Estimations of V/U and V/t_2 magnitudes in $(TMTTF)_2PF_6$ obtained from quantum chemistry calculations and from optical conductivity [4,12] yields values for V/U in the range 0.4-0.5 and for V/t_2 in the range of 2-3 manifesting the essential role played by the long range Coulomb interaction in this compound. Hereafter we present results of conductivity and dielectric permittivity measurements of $(TMTTF)_2PF_6$ which provide some evidence of a charge modulated state (analogous to Wigner crystal) resulting from electron-electron charge correlation below T_ρ.

II. EXPERIMENT

We have studied $(TMTTF)_2PF_6$ samples originating from two batches. The crystals have been prepared using standard electrochemical procedures [16]. Electrical contacts were prepared by first evaporating gold pads on nearly the whole surface of the sample's ends on which thin gold wires were attached afterwards with silver paste. We have carried out the measurements of complex conductance $G(T, \omega)$, using an impedance analyser HP 4192A in the frequency range 10^3–10^7 Hz and in the temperature range 4.2–295 K. The amplitude of the ac voltage applied to the sample was within the linear response and typically 30 mV/cm. We have noticed that the cooling rate had a significant effect on the results of our measurements, much more important than in the case of $(TMTTF)_2Br$ for instance [17]: at a cooling rate above 0.5 K/mm, cracks appear as seen in jumps in the temperature variation of G. However with a slow cooling rate around 0.2 K/mm and along temperature stabilisation before performing measurements, we succeeded in recording the temperature dependences of real and imaginary parts of G without any jumps for 3 samples. These samples have a length of 3–4 mm, a cross-section about $2 \times 10^{-5} - 10^{-4}$ cm^2 and a room temperature conductivity ~ 40 Ω^{-1}cm^{-1}. The results obtained for these 3 samples being qualitatively similar and we will present the data for two of them (referred as samples 1 and 2).

Fig.1 shows the variation of the conductance $G(T)$ of sample 1 normalized by its maximum value G_m as a function of the inverse temperature. The detailed $G(T)$ dependence near the room temperature is shown in inset (a) of Fig.1. With decreasing temperature, the conductance of $(TMTTF)_2PF_6$ first grows up to a maximum at $T_\rho = 250$ K as previously reported in [2,3]. Below T_ρ, the decrease of $G(T)$ in the temperature range 200–70 K follows an Arrhenius type behavior with an activation energy $\Delta\rho \simeq 300$ K. The value of this activation energy is in good agreement with the evaluation of charge gap in [11]. It was shown that $\Delta\rho = 1/4(t_1 + t_2)$ which provide $\Delta\rho \simeq 300$ K for $(TMTTF)_2PF_6$. At the same time this magnitude of energy gap is two times smaller than the value reported in a previous publication [2]. This difference can be a result of the gap determination in [2] from $G(1/T)$

dependence obtained by averaging of $G(1/T)$ dependencies from several different samples with jumps of G due to cracks. The jump-like decrease of conduction at every crack results in more steep averaged $G(1/T)$ dependence and accordingly in more higher gap magnitude. The small cooling rate enables us to avoid cracks and to determine more accurately the energy gap magnitude which agrees with theoretical evaluation [11].

At lower temperature we observed a bend on the $G(1/T)$ dependence near 70 K, i.e. G begins to decrease more faster (activation energy $\approx$ 380 K) with a following gradual transition to a new activation regime at temperatures below 25 K. Detailed measurements of sample 2 show that the decrease of G is thermally activated between 4.2 K and 20 K with an activation energy $\simeq$ 36 K. This energy gap satisfied the BCS-like relation $\Delta = 1.75kT_{\mathrm{SP}}$ with $T_{\mathrm{SP}} \simeq$ 20 K as previously shown in the temperature dependence of the EPR spin susceptibility and the nuclear relaxation rate T_1^{-1} [18].

It can also be seen in Fig.1 that the frequency dependence of $G(1/T)$ become noticeable below 70 K with a frequency dispersion growing at lower temperature. For showing more precisely the particular points on the $G(1/T)$ variation we draw in inset (b) of Fig.1 the temperature variation of the logarithmic derivative which was reproducible for our three samples. The decrease of G near $T \simeq$ 70 K may indicate the beginning of a transition into some new ground state. Two additional small minima in $d \log G/d(1/T)$ are also visible near 140 K and 100 K (inset (b) in Fig.1.

The temperature variation of the real part of the dielectric permittivity $\epsilon'(T)$ of sample 1 in the frequency range $10^3 - 5 \times 10^6$ Hz is shown in Fig.2. Between 300 K and 220 K, the magnitude of ϵ' is below the background level determined by the resolution of our measurements in this temperature range. The growth of ϵ' is noticeable below $\simeq$ 200 K and frequency independent down to $T \simeq$ 110 K. Below this temperature a significant frequency dispersion occurs as seen in Fig.2: at a given frequency $\epsilon'(T)$ goes through a maximum before falling down. With decreasing frequency, the amplitude of the maximum of $\epsilon'(T)$ is larger and the maximum position on the temperature scale shifts to lower temperature. This behavior is qualitatively similar to critical slowing down phenomena near a phase transition.

The $\epsilon'(T)$ curves for samples 1 and 2 are shown in inset of Fig.2 in a double logarithmic scale, manifesting their qualitative similarity. In the temperature range 200–70 K, the $\epsilon'(T)$ dependence can be described by the power law: $\epsilon'(T) \sim T^{-\alpha}$ with $\alpha \simeq 1/3$. While $\epsilon'(T)$ is decreasing from 70 K down 10 K, a small bump in $\epsilon'(T)$ can be seen near $\simeq 35$ K.

The frequency dependencies of the conductance, of the real part ϵ' and of the imaginary part ϵ'' of the dielectric permittivity of $(TMTTF)_2PF_6$ have a form similar to those we previously measured on other 1D organic compounds [17,19]. As usual, the frequency, f_m, corresponding to the maximum of $\epsilon''(T)$ corresponds to some mean value of the relaxation time $\tau = 1/2\pi f_m$ of charge polarization. The variation of τ with the inverse temperature is drawn in Fig.3 for sample 1 in the temperature rangee 95–35 K: for $60 < T < 95$ K, $\tau(1/T)$ is thermally activated with an energy activation of ~ 650 K; but, at lower T, 35 K$< T <$60 K, the activation energy is smaller, ≈ 380 K, the same as the activation energy of the conductivity in same temperature range.

III. DISCUSSION

As follows from published data [1,18] and from our experimental results, $(TMTTF)_2PF_6$ can be characterized by two distinct energy scales: temperature $T_\rho = 250$ K corresponding to the conduction maximum and $T_{SP} \simeq 20$ K corresponding to the transition into the spin-Peierls state. If one will consider the temperatures $T_{SP} < T < T_\rho$ as a range of simple localization of charge carriers [1], one could try to explain the observed growth of ϵ' as a result of the growth of $2k_F$ CDW fluctuations when approaching T_{SP} [20]. As was mentioned in [8] the temperature range of fluctuations near the spin-Peierls transition can be wide enough and reach $\sim 3T_{SP}$. It means that in $(TMTTF)_2PF_6$ the manifestation of the fluctuations can be noticed beginning from $T = T_{SP} + 3 \times T_{SP} \simeq 80$ K, temperature at which $2k_F$ fluctuations have started to be really observed [20]. However as can be seen from Fig.2 the ϵ' growth begins nevertheless not from 80 K but from $\simeq 200$ K. For frequencies above 10^6 Hz this ϵ' growth is rather achieved at 80 K. This dismatching in the temperature ranges for

occurence of $2k_F$ fluctuations and the ϵ' growth makes difficult the explanation of ϵ' growth as a result of $2k_F$ CDW fluctuations. In the same temperature range $50 - 200$ K, EPR susceptibility χ decreases monotonously without any maximum [18].A small maximum on $\chi(T)$ dependence was observed near 40 K with a following decrease of χ as a result of the transition to the spin-Peierls state. Such considerable qualitative difference between $\epsilon'(T)$ and $\chi(T)$ dependences confirms the existence of spin-charge separation in $(TMTTF)_2PF_6$ salts.

We tentatively ascribe the frequency and temperature dependences of ϵ' of $(TMTTF)_2PF_6$ in the temperature range $T_{SP} < T < T_\rho$ as related to the charge induced correlation phenomena discussed above. Taking into account only on-site interactions in the Hubbard model for half-filled band, the commensurate charge induced superstructure ($4k_F$ CDW) is strictly linked to the host lattice. In such a case the possibility of polarization of the superstructure, i.e. its shift with respect to the host lattice, is small and consequently one would expect a low magnitude of the dielectric permittivity. Ground state with Mott-Hubbard gap and appropriate charge localization have been realized in 3D semiconductors [21]. In such compounds ϵ' is in the order of 10, a typical value for usual semiconductors, while in our samples of $(TMTTF)_2PF_6$ the ϵ' magnitudes amount by several orders of value larger (Fig.2).

As explained above, long range Coulomb interaction of sufficient strength and appropriate charge induced correlation may lead to a superstructure with charge disproportionation corresponding to a $4k_F$ CDW as in a Wigner crystal. For $(TMTTF)_2PF_6$ this charge disproportionation can be evaluated on the base of calculations in [13] taking into account the estimated magnitude of the reduced near-neighbor Coulomb interaction $V/t_2 \simeq 2$ [4,12].For such a V/t_2 value we estimate the charge disproportionation as about 1:3. Such a degree of disproportionation and the possibility of its variation with temperature [4], provide some evidence that this charge superstructure is probably more soft, more weakly connected to the host lattice and consequently more easily polarizable than in the case of only on-site interaction. We ascribe the large magnitude of the dielectric permittivity, which we have found

out below T_ρ, to the collective response of such charge superstructure of Wigner crystal type with charge disproportionation formed in $(TMTTF)_2PF_6$. Indeed, as can be seen from Fig.2 in the temperature range above T_ρ the ϵ' magnitude does not exceed the background level. Its noticable growth begins below 200 K when, as we considered, the growing of this Wigner type CDW superstructure begins to determine the kinetic properties of the compound. The ϵ' growth with temperature decreasing is probably associated with the gradual enhancement of the CDW superstructure. Possible reasons for such an enhancement can be the growth of intrachain charge induced correlations as well as the growth of interchain interactions. Both of them favour the three dimensional ordering of the CDW superstructure, i.e. the formation of a 3D electronic crystal. The maximum value of ϵ' amounts to $10^5 - 10^6$, 2 or 3 orders of magnitude lower than the ϵ' values in incommensurate charge [22] and spin [19] density wave below their transition temperature. However the magnitude of ϵ' in $(TMTTF)_2PF_6$ is nearly comparable with that in $(TMTTF)_2Br$ [17].

According to X-ray measurements [20], diffuse $2k_F$ scattering grows critically in $(TMTTF)_2PF_6$ below ~ 80 K which originates from the gradual enhancement of spin induced electron-electron correlation of antiferromagnetic type. Due to the growth of the electron-phonon interaction and of the increasing of the interchain interaction, these $2k_F$ spin induced correlations diverge below T_{SP} resulting in the condensation of an ordered spin-Peierls state with a $2k_F$ superstructure.

The opening of the spin-Peierls energy gap and the two-fold commensurability of the superlattice lead to the freezing of charge polarization degrees of freedom and consequently to the sharp decrease of ϵ'. The slowing down behavior of ϵ' and the temperature dependence of the relaxation time (Fig.3) also indicate the lattice involvment (i.e. heavy molecules) in the relaxation process.

IV. CONCLUSION

In conclusion, our measurements of the complex conductivity of $(TMTTF)_2PF_6$ show the main following features: 1) development of a charge energy gap the magnitude of which corresponds to theoretical evaluations in the frame of extended Hubbard model; 2) existence of peculiarities on $G(1/T)$ dependence, for example, a minimum of the logarithmic derivative near 60 K; 3) in the same temperature range, finding of a huge maximum of the real part of the dielectric permittivity (up to 10^6) with a slowing down behavior with decreasing temperature while the magnetic susceptibility does not show any significant variation, which corresponds to large charge polarization simultaneously with spin-charge separation; 4) considerable difference between the temperature dependence of the dielectric permittivity and $2k_F$ diffuse X-ray scattering.

All these features seem to confirm the possibility of the formation in the temperature range $T_{SP} < T < T_\rho$ of a charge ordered state with a high polarizability. On the basis of our experimental results and some theoretical approaches we consider that we consider that the huge amplitude of the real part of the dielectric permittivity of $(TMTTF)_2PF_6$ can hardly be provided by a Mott-insulator. On the contrary, we argue that this large dielectric polarizability reflects the collective response of $4k_F$ charge density wave of Wigner crystal type due to long range Coulomb interaction and electron-electron correlation. Recently charge disproportionation [23] and $4k_F$ superlattice [24] have been reported from NMR and X-ray measurements in a 1/4 filled one-dimensional organic compound $(DI\text{-}DCNQI)_2Ag$ without dimerization.

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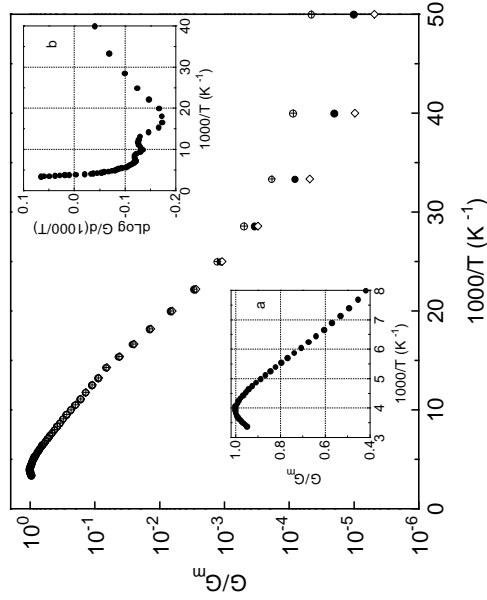[24] Y. Nogami, K. Oshima, K. Hiraki, and K. Kanoda, J. Phys. IV (France) **9**, Pr10–357 (1999).

FIG. 1. Variation of the real part of the conductance G (sample 1) normalized to its maximum G_m as a function of the inverse temperature at frequencies (in kHz): $\Diamond$ 10, $\bullet$ 100, $\oplus$ 1000. Inset (a): details of the temperature dependence of G/G_m near the maximum. Inset (b): temperature dependence of the logarithmic derivative $d\log G/d(1000/T)$.
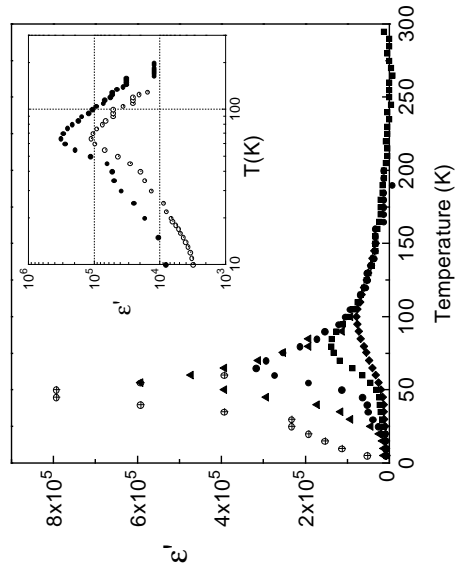
FIG. 2. Temperature dependence of the real part of the dielectric permittivity ϵ' (sample 1) at frequencies (in kHz): $\oplus$ 1, $\blacktriangle$ 10, $\bullet$ 100, $\blacksquare$ 1000, $\blacklozenge$ 5000. Inset: temperature dependence of ϵ' for sample 1 ($\bullet$) and sample 2 ($\odot$) at 100 kHz in a double logarithmic scale.
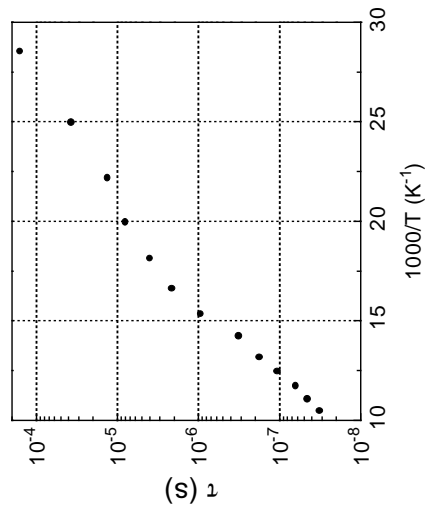
FIG. 3. Temperature dependence of the relaxation time τ of the dielectric relaxation (sample 1).